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S. W. STRATTON, DIRECTOR

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BY

F. L. MOHLER, Physicist
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Bureau of Standards

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By F. L. Mohler and Paul D. Foote

ABSTRACT

Potentials required to excite successive types of radiation in a low-pressure Wehnelt arc have been measured by observing the photoelectric effect of the arc radiation on other electrodes within the same tube. Critical radiating potentials for 11 gases and vapors have been measured in a range from 17 to 500 volts. The corresponding limiting spectral frequencies ranging from $\lambda=700$ to $\lambda=25$ *A* include the softest characteristic X-rays for all the elements considered. Critical potentials corresponding to the principle *L* series limit of sodium, magnesium, phosphorus, sulphur, and chlorine have been measured. A softer and fainter *L* limit has also been discovered in these elements. The *K* series limits of carbon, nitrogen, and oxygen have been identified, as well as the softest X-ray limits (*M* series) of potassium. Measurements of radiation from four carbon compounds gave identical results for the *K* limit of carbon.

Experiments with radiation from solids indicate the existence of soft characteristic X-radiation, with no measurable general radiation under the best vacuum conditions. Nickel shows radiation starting at 80 volts.

CONTENTS

I. INTRODUCTION

The present paper is concerned with measurements of the potentials required to excite successive types of radiation in gases and vapors by electron impact. A knowledge of the physical conditions whereby different kinds of radiation may be

stimulated is of great interest in its bearing upon the various theories of atomic structure and is most essential for the rational development of certain technical engineering problems of immediate importance. The energy transformations involved in electron collision are as follows: The kinetic energy $\frac{1}{2}mv^2$ of the colliding electron is equal to Ve, where V is the potential difference through which the electron has fallen. At any potential greater than the first ionization point, collision with an atom may result in the ejection of an electron from the atom at the expense of part or all of this kinetic energy. The positive ion upon recombination with another electron will emit radiations of frequencies ν_n related to the energy E required to eject the electron as follows:

$$E = \Sigma h(\nu_1 + \nu_2 + \nu_3, \text{ etc.})$$

The highest possible frequency ν is such that $h\nu = E$. The least potential V required to eject the electron by collision and the limiting frequency ν of the resulting radiation are thus proportional, viz:

$$Ve = h\nu \text{ or } \lambda(A) = \frac{12\,345}{V\,(\text{volts})}$$

The limit ν is found to be the convergence frequency of a series of absorption lines, in all cases where the series relations are known, and in X-ray spectra it defines the edge of an absorption band. Thus either from spectroscopic measurements of the limiting frequencies of different types of radiation or from measurements of the least potential required to excite the radiation, the energy levels of the various atomic configurations may be determined.

The following transitions in the type of electron collisions take place. Above the first ionization potential one valence electron may be ejected and the arc spectrum is emitted upon recombination. At successively higher potentials two or more electrons may be ejected, with subsequent emission of the spark spectra of first or higher orders.

The electronic orbit in the atom nearest the nucleus is designated as the K orbit. Outside of this are the L, M, N, etc., orbits of successively greater diameter. Ejection of one of these electrons subsequently gives rise to the emission of X-ray spectra. If the removal is from the K ring, different lines of the K series are produced when the ejected electron returns to its equilibrium position, and similarly for the other rings.

In part because of the experimental limitations to spectroscopic analysis, but little work has been done in the investigation of the radiation from the outer X-ray orbits. The spectrum range from $\lambda = 0.1$ to $\lambda = 12$ *A* or from 100 000 to 1000 volts has been studied by the crystal spectrometer. The range of the grating spectrograph has in recent years been extended from over 20 000 *A* to less than 200 *A*, though data are very incomplete below 1200 *A*. It is, however, with this comparatively small range from 1200 to 12 *A* or from 10 to 1000 volts that all the outer X-ray orbits and probably most of the spark spectra are concerned. No X-rays have been observed from elements in the first row of the periodic table and only the *K* series in the second and third rows. It is to be expected that for the heavy elements, besides the observed *K*, *L*, and *M* series, *N* and *O* series exist, all falling in the spectral range heretofore inaccessible.

The possibility of measuring the potentials required to excite these radiations and by purely electrical measurements supplanting the meager spectroscopic data is suggested by the success of various investigators in determining resonance potentials by the radiation method.[1] In this is observed the photoelectric effect of a low-pressure Wehnelt discharge on electrodes within the same vacuum tube but electrically shielded from both positive and negative ions in the arc. The method offers a means of detecting radiation shorter than about 3000 *A*, including the region to which all materials are opaque.

An obvious difficulty in measuring the X-ray excitation potentials from a discharge in a gas is that the X radiation is superposed on the arc and spark spectra. This would not be true if the soft X-rays were obtained from solids, as in the ordinary X-ray tube. Numerous attempts of observers in the past to apply this latter method[2] have failed, however, to show any convincing evidence of radiation characteristic of the anode material. They observed, apparently, general radiation starting at low voltage and increasing gradually with increased potential. Some experiments of the authors on radiation from solids were more successful, a brief statement of which is given in the latter part of this paper. Trouble with surface contamination of the anode, together with the requirements of the highest possible vacuum and sensitive current measurement, made the experiments very

[1] A few of the papers on this are Davis and Goucher, Phys. Rev., 10, p. 101, 1917; Horton and Davies, Proc. Roy. Soc., 95, p. 408, 1919; Mohler and Foote, B. S. Sci. Paper 400, 1920.

[2] Thomson, J. J., Phil. Mag., 28, p. 620, 1914; Laird, Ann. d. Phys., 46, p. 605, 1915; Laird and Barton, Phys. Rev., 15, p. 297, 1920; Dadourian, Phys. Rev., 14, p. 234, 1919.

difficult. It was found that in the work with vapors and gases the superposition of arc and spark radiations did not under suitable conditions mask the higher radiation potentials.

Since this work was undertaken other observers have announced fairly definite evidence of characteristic X radiation in this inaccessible range. Hollweck[3] has found evidence of selective absorption of carbon for general radiation from a solid anode. Kurth[4] has announced the measurement of the potential required to excite characteristic X-rays in the range from 12 to 400 A for five different elements used as solid targets.

In this connection it should be added that Millikan has found some of the longest X-ray emission lines in photographs of hot spark spectra with a vacuum grating spectrograph.[5]

No previous experiments have shown evidence of characteristic soft X-rays from gases. Whiddington[6] showed that there was radiation from air of a frequency range corresponding to 100 to 200 volts. The results of Richardson and Bazzoni,[7] although negative in this respect, are interesting because of the method used. They measured the maximum frequency radiated in a low-pressure arc by observing the maximum velocity attained by photoelectrons excited by this radiation. The velocity was measured by the curvature of the electron paths in a magnetic field and the frequency was computed from the Einstein equation. No radiation of frequency higher than the limit of the arc spectrum was found but the method lacked sensitivity. This at least suggests the possibility of not only measuring the potentials required to excite soft X-rays but of estimating the frequency emitted as well, by purely electrical methods.

In the present work the identification of the critical potentials observed as due to X-ray excitation rests on the agreement of observed values with the limits computed from X-ray data.

II. APPARATUS AND METHODS

Fig. 1 shows diagrammatically the arrangement of electrodes and electrical connections used to measure the radiation from arcs in gases. The electrodes *B C D* are concentric cylinders surrounding the hot wire cathode *A*. The electron current is maintained by a potential *V* between *A* and *B* and the radiation resulting

[3] C. R., 171, p. 849, 1920; 172, p. 439, 1921.
[4] Abstract, Phys. Rev., 17, p. 528, 1921; also paper read before Physical Society in April, 1921.
[5] Paper read before Nat. Acad. Sci., April, 1921, The authors lack complete data.
[6] Camb. Phil. Soc., 17, p. 144, 1913.
[7] Phil. Mag., 34, p. 285. 1917.

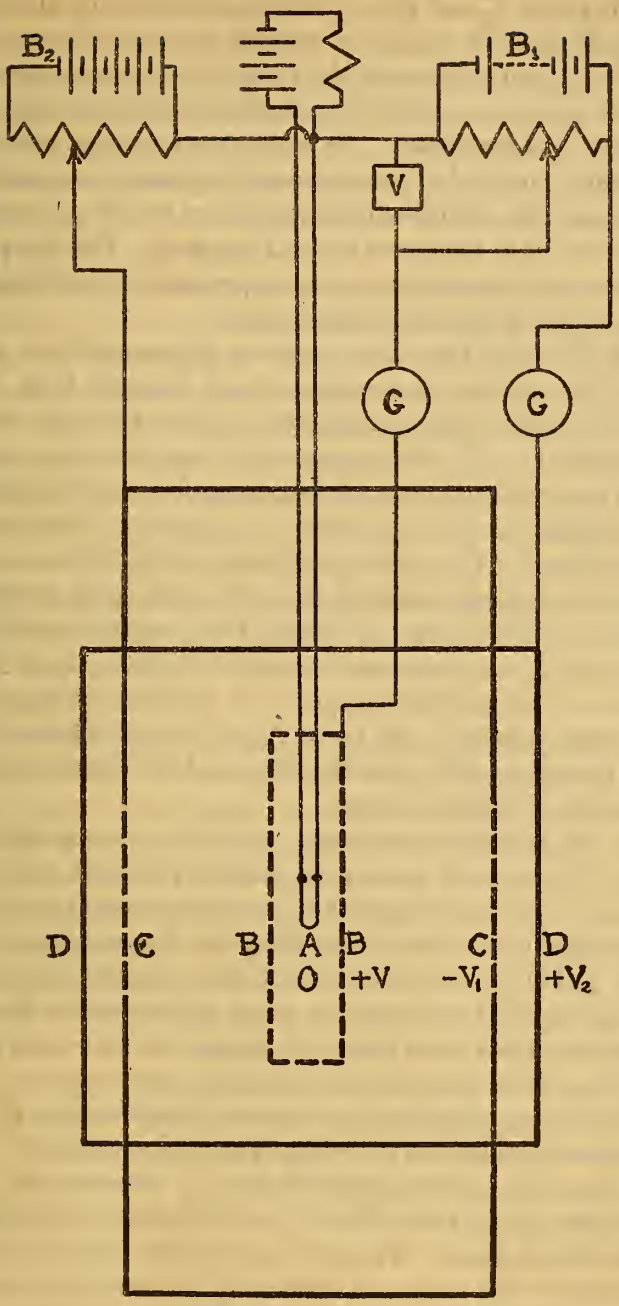

FIG. 1.—*Electrodes and electrical connections*

from electron collisions with the gas gives rise to a photoelectric current between C and D. It is essential that the electrons from the cathode actually acquire a velocity equivalent to the potential V and this is not in general the case with a current between two electrodes in a gas, on account of the loss of velocity when electrons collide with gas molecules. To insure the electrons receiving their full velocity, the grid B was mounted as closely as possible to the cathode and the gas pressure adjusted so low that nearly all collisions occurred in the space beyond the grid. This is a precaution of fundamental importance in any experiments involving the effect of potential on discharge through gases.

The shielding of the outer electrode is accomplished as follows: Consider the cathode at o potential and the grid B at $+V$. The outer grid, which almost completely incloses the inner one, is kept at a potential $-V_1$, thus preventing electrons from reaching it. Positive ions will pass through but can not reach the outer plate D when maintained at a potential $+V_2$ greater than the highest value of V used. The potential difference $V_1 + V_2$ between C and D draws photoelectrons emitted from the outer grid to the plate.

Various evident means of testing the complete shielding of the outer electrode were frequently applied. For example, the radiation current will approach zero at low pressure while a stray electron current around C will not. Again, a stray current from the arc will change rapidly with the potential of C, while this has little effect on the radiation current.

There are several connections possible for measuring the ionization. The method most used was to put both the outer grid and plate at $-V_1$ and measure the positive current reaching them. The photoelectric current from the plate is superposed on the ion current, but as radiation currents were usually about one-hundredth as large as the positive currents this factor is negligible. The vacuum tubes were similar in design to those used previously in studying resonance potentials in gases and vapors.[8] For work with the vapors of sodium, potassium, magnesium, phosphorus, and sulphur tubes of the following type were employed:

The electrodes were suspended from a water-cooled metal top into a Pyrex glass tube about 7 cm in diameter and 40 cm long, closed at the bottom. The substance to be boiled was placed in the bottom of the tube and heated by an electric furnace. Care was taken in the suspension of the electrodes that they did not touch the hot glass walls and that the glass insulation in the top

[8] Mohler and Foote, B. S. Sci. Papers 400 and 403.

plate was shielded by outer tubes from the condensing vapor. Electrodes of sheet nickel and fine platinum gauze were used for these elements except magnesium, for which nickel gauze was employed. The outer grid was a cylinder of sheet nickel, closed at the bottom, with a zone of platinum gauze in the side. Cathodes were of oxide-coated platinum strips or of bare tungsten wire. The vapor density was controlled by varying the temperature of a furnace or, in the case of phosphorus, a water bath around the bottom of the vacuum tube.

The tube used for the carbon compounds and air was much smaller, about 4 cm in diameter, with electrodes smaller in proportion and all of platinum. The tube was of Pyrex glass with tungsten seals. Cathodes were either of tungsten or oxide-coated platinum. Gases were usually streamed through the tube through a plug of plaster of Paris. The flow was varied by changing the pressure on the high-pressure side of the plug. Liquid-air traps on each side of the discharge tube condensed all vapors. CCl_4, however, was streamed through the tube from a container at about $-70°$ C on one side to a trap in liquid air on the pump side. The temperature controlling the vapor pressure was maintained by a bath of petroleum ether with enough CCl_4 in it to make a slush at about $-60°$ C.

Several mercury-vapor pumps in series maintained the vacuum, and pressures were read on a McLeod gage sensitive to slightly less than 0.0001 mm of mercury. The electrical connections are shown in Fig. 1. The battery B_1, which supplied the arc current, was always made somewhat larger than the potential range to be studied. It is seen from the diagram how the plate is maintained at a constant potential $+V_2$ greater than V by the same battery. The retarding field maintained by B_2 was usually about 10 volts. The potential V across the arc was measured by a voltmeter with a 150-volt scale and the range increased as desired by calibrated series resistances. The current from the cathode, usually about 1 milliampere, was measured by a microammeter with a shunt resistance to regulate its sensitivity. The current to the outer plate was measured by a galvanometer, the sensitivity of which was likewise reduced by a shunt. It is interesting to note that we found the limit of sensitivity 10^{-10} amperes ample for all the work on gases and vapors.

In taking readings, for each setting of the voltage V the photoelectric current and also the current from the cathode were measured. The photoelectric current was then divided by the cathode

current and this ratio plotted against the potential V. As the radiation intensity is proportional to the cathode current for any one potential, this ratio eliminates the different characteristics of the cathode emission under changing conditions, and hence slow variations during a series of readings will not modify the results obtained. It happens that the resulting curves show nearly a straight-line relation between the photoelectric effect and the potential across the arc, with a change in slope occurring at critical potentials. The accuracy of this straight-line relation was well shown in some curves obtained in potassium. The points fall on a straight line from 23 to 140 volts, with no deviation greater than the probable experimental error of about 2 per cent. The physical significance of this property is not evident, for many factors enter, and the linear relationship is probably only an approximation. The usefulness of the relation in measuring critical potentials is, however, apparent as the critical points are the intersections of straight lines.

For an accurate determination of critical potentials it is necessary to know the correction term to be added to the applied voltage to give the effective potential through which electrons fall. This initial potential correction due to the resultant effects of potential drop along the cathode, contact difference in potential and temperature distribution of velocities of emitted electrons is usually of the order of ± 1 volt. The correction was found from the difference between the observed potential at which ionization began and the value of the ionization potentials as given in previous publications of the authors. As an accuracy of 1 volt was all that was obtainable, no great precision was required in applying such corrections. For the measurements at high voltage the only correction made was for the voltage drop across the cathode where this was large.

III. RESULTS

The following pages give results obtained for critical radiating potentials in 11 elements and compounds. Figs. 2 to 7 give typical curves and the accompanying tables the conditions of measurement and other remarks on the curves illustrated. An analysis of *all* the curves obtained which showed inflections suitable for measurement is also included. Particular care was required in some cases to secure conditions which gave definite inflections, and often many useless curves were taken before these conditions were found. Potential current readings were more or less limited to a range around the predicted potential necessary

for X-ray excitation. Thus it has happened in some instances that radiation potentials at lower voltages have been passed over entirely or only approximately located.

As X-ray excitation requires ionization of the atom, critical potentials should be indicated by an increase in the positive current as well as radiation. Careful measurements of ionization currents were made in sodium and potassium and under certain conditions the predicted effect was found as shown in some of the accompanying curves. This measurement proved more difficult than the radiation method, as the curves were never straight lines, so that in other elements ionization curves were taken only at low voltage to measure the initial potential correction.

In the statement of the mean result of observations the average precision of the observed points is given. This is doubtless always less than the probable error, but cases where systematic errors are suspected are noted. In several instances where uniformity of data permitted we have taken a number of series of readings, averaged them, and then drawn a curve through the mean points. This gives a check on the mean of separate series of readings and at least in two cases shows that what appeared to be one inflection in the separate curves was actually two, one of which was faint. As a result the mean of separate curves gave an inflection which did not agree in position with either of the inflections in the mean curve but was between the two and closer to the stronger, as should be expected.

1. POTASSIUM

The radiation potentials in potassium above the first ionization point are shown more strikingly than in any other element. There is a strong inflection at 23 volts and with higher vapor pressures a fainter inflection at 19 volts. Measurements to 140 volts show no points above 23. The pronounced change in slope does not necessarily indicate that the radiation above 23 volts is intense compared to the arc radiation, but is probably due to the fact that the arc radiation, with its high frequency limit at $\lambda = 2857$, is very ineffective in producing photoelectrons from platinum. The photoelectric current measures intensity only when the spectral distribution of energy is unchanged, so that the change in slope at critical potentials is not simply related to the change in intensity. As two separate inflections were found in only 6 of the 15 curves considered, it is probable that the singly observed point at 23.3 volts was in some cases due to the overlapping effect of the two and the mean value for the upper point is

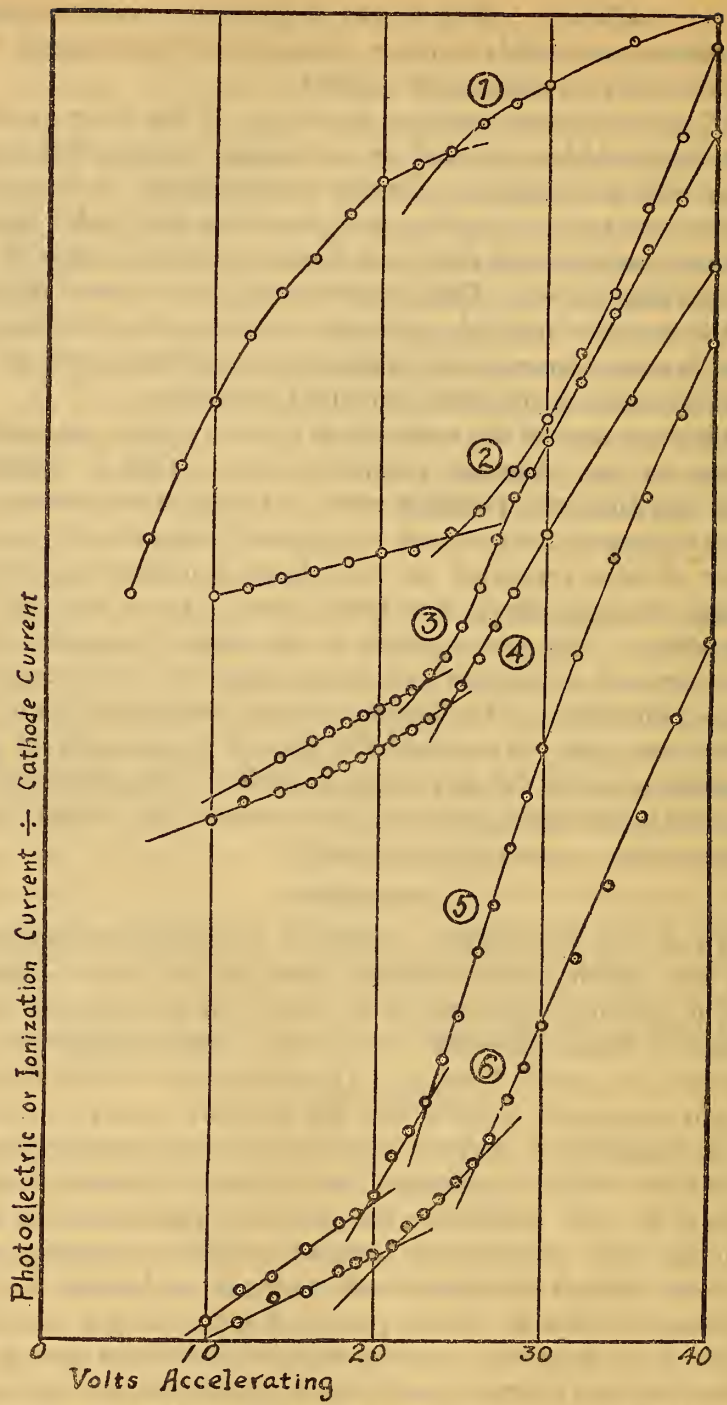

FIG. 2.—*Current-voltage curves in potassium; ionization and radiation*

accordingly too low. This may account for the rather large mean error in determining an apparently very sharp point of inflection, as shown in Table 1.

TABLE 1.—Data for Potassium Curves in Fig. 2

Curve	Temperature	Observed points	Initial potential correction
	°C	Volts	Volts
No. 1 ionization	235	24	−1
No. 2 radiation	230	24	−1
No. 3 radiation	170	23	−1
No. 4 radiation	180	24	−1
No. 5 radiation	225	19. 5 23	−1.2
No. 6 radiation	240	21. 26	−1.2

Results from 15 curves (1 ionization and 14 radiation) show radiation and ionization at 23.3, mean error ±1.0; 6 curves show a lower point also at 19.3, mean error ±0.7.

2. SODIUM

Higher radiation potentials in sodium were not as marked as with potassium. They appeared sharper as the vapor density was increased, but then the currents became unsteady. Some curves at higher temperature show a marked curvature concave to the voltage axis instead of a straight line. It required long pumping to eliminate the gas evolved, and the inflection at 17 volts was at first ascribed to molecular hydrogen, which ionizes at 16 volts. It did not disappear, however, as the vacuum improved even after several days of heating, with the pumps running. Other evidence will be given later that this may be a sodium point.

TABLE 2.—Sodium Curves in Fig. 3

Curve	Temperature	Observed points	Correction
	°C	Volts	Volts
No. 1 ionization	335	38	−2
No. 2 ionization	268	36	0
No. 3 ionization	277	34	−1
No. 4 radiation	250	32	0
No. 5 radiation	315	35	0
No. 6 radiation	325	34	0
No. 7 radiation	285	16 35.5	0
No. 8 radiation	273	37	0
No. 9 radiation	285	38	−2
No. 10 radiation	280	37	−2
No. 11 radiation	255	37	−2

Results from 20 curves, 3 ionization and 17 radiation. Radiation and ionization at 35 ±1.4 volts. Eight curves showed radiation at 17 ±1.5 volts.

3. MAGNESIUM

The vapor pressure required to show higher critical potentials in magnesium necessitated a temperature of about 600° C, and the thermionic leak from the hot electrodes limited the precision.

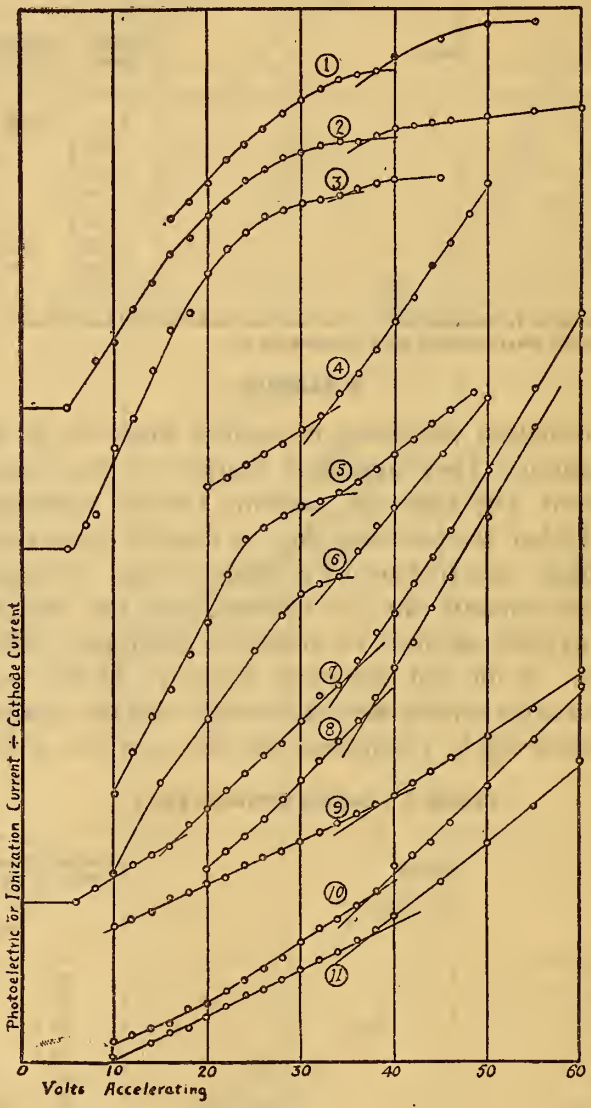

FIG. 3.—*Current-voltage curves in sodium; ionization and radiation*

The results appear more precise, however, than with sodium. The marked curvature between 10 and 25 volts is undoubtedly due to double ionization. Theory[9] indicates that 22.6 volts are

[9] Transitions in the magnesium spectrum are described in detail in a paper by Foote, Meggers, and Mohler, to appear in Phil. Mag.

required to eject both electrons from a neutral atom and 14.95 volts to eject the second electron from a singly ionized atom. Conditions were not favorable for the measurement of these points. There may be a considerable systematic error in the 33-volt point, as the interval in readings below 30 volts was too large. The existence of this inflection was not suspected until all the data had been obtained.

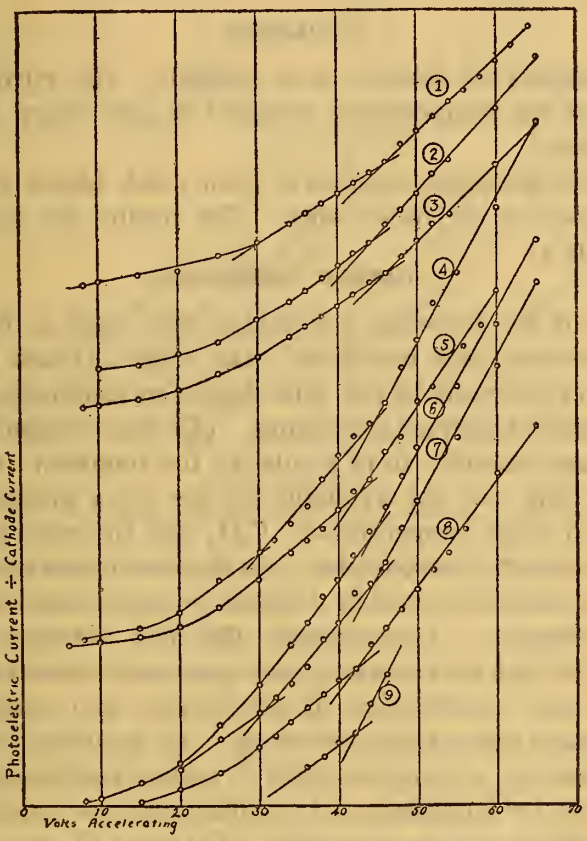

FIG. 4.—*Radiation-voltage curves in magnesium*

TABLE 3.—Magnesium Curves in Fig. 4

Curve	Temperature	Observed points	Curve	Temperature	Observed points
	°C	Volts		°C	Volts
No. 1	600	30 46	No. 6	560	44
No. 2	610	44	No. 7	560	31 44
No. 3	590	46	No. 8	615	42.5
No. 4	590	31 45	No. 9	560	42
No. 5	615	43			

Initial correction in each case +1.6. Results from 11 curves show inflection at 45.8 ±0.8; 7 curves show point at 33.3 ±1.2. A curve through the mean of 7 series of readings gives points of inflection at 47.0 and 33.6.

4. PHOSPHORUS

Results were obtained with yellow phosphorus at temperatures below 50° C. Currents were very steady and results at least for the 126-volt point fell in a small voltage range. Critical potentials at lower voltages were evident in some curves, but measurements were largely limited to a range above 80 volts. Polyvalent atoms must have many radiation potentials due to multiple ionization.

5. SULPHUR

Measurements in sulphur were difficult. The currents were unsteady at the temperatures required to give sharp inflections in the curves.

The vapor pressures must have been much higher than those used in most of the other work. The results are summarized under Table 4.

6. CARBON COMPOUNDS

These and the following substances were used in the second type of vacuum tube described. The gases CO and CO_2 were usually kept stagnant in the tube during measurements but the gas was renewed between each series. CCl_4 was streamed through the discharge chamber from a tube at the temperature given in Table 5. Data are not available for the vapor pressures corresponding to these temperatures. C_2H_2 and the other gases were streamed through a porous plug. In the case of the carbon compounds we were interested in a higher voltage range than in the foregoing elements. Consequently the field between the electrodes was so high that sparking took place under some conditions. C_2H_2 was most troublesome in this respect and measurements could be made only at low pressures. The resulting curves were least satisfactory of those obtained in carbon compounds. None were suitable for reproduction, but inflections were measurable on some and the results are tabulated. CO and CCl_4 also showed a tendency to spark when the pressure was too high. The CO measurements showed rather unsteady currents, but sharp inflections, while the CO_2 measurements were most steady, but inflections were less pronounced. CCl_4 showed inflections ascribed to chlorine as well as to carbon, but in all other cases the inflections seem to be at the same points. Apparently they are due to radiation from carbon atoms. Only a few measurements were made in a low-voltage range. The 75 volts inflection is sharp.

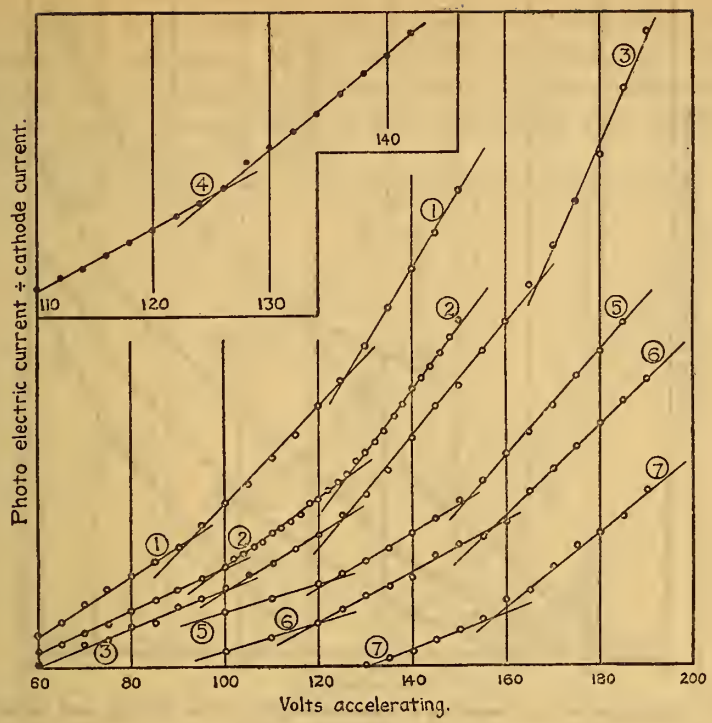

FIG. 5.—*Radiation-voltage curves in phosphorus and sulphur*

TABLE 4.—Phosphorus and Sulphur Curves in Fig. 5

Curve	Temperature	Observed points	Remarks
	°C	Volts	
No. 1 phosphorus	25	94 126	
No. 2 phosphorus	40	93 126 165	Initial correction +1 in each case
No. 3 phosphorus	40	100 125	
No. 4 phosphorus		125.5	Mean of 6 series
No. 5 sulphur		122 153	Do.
No. 6 sulphur	210	120 156	Initial correction −1 in each case
No. 7 sulphur	210	157	

PHOSPHORUS

Results from 14 curves show inflection at 126 ±0.9 volts corrected; 8 curves show a point at 99 ±2; 7 curves show a point at 163 ±2; 2 curves show a point at 109 ±1.

A mean of 7 series at 5-volt intervals gives points at 93, 111, 127, and 160. Probably the point observed in separate curves at 99 is due to the superposed effect of faint inflections at 111 and 93. The lower point is probably at 95 ±5 volts. The mean curve of 6 series at 2-volt intervals (Fig. 5, No. 4, upper scale) gives 125.5 volts.

SULPHUR

Results from 15 curves show inflections at 152 ±2.5 and at 122 ±1. A curve through the mean points of the 6 best series gives 152 and 121.

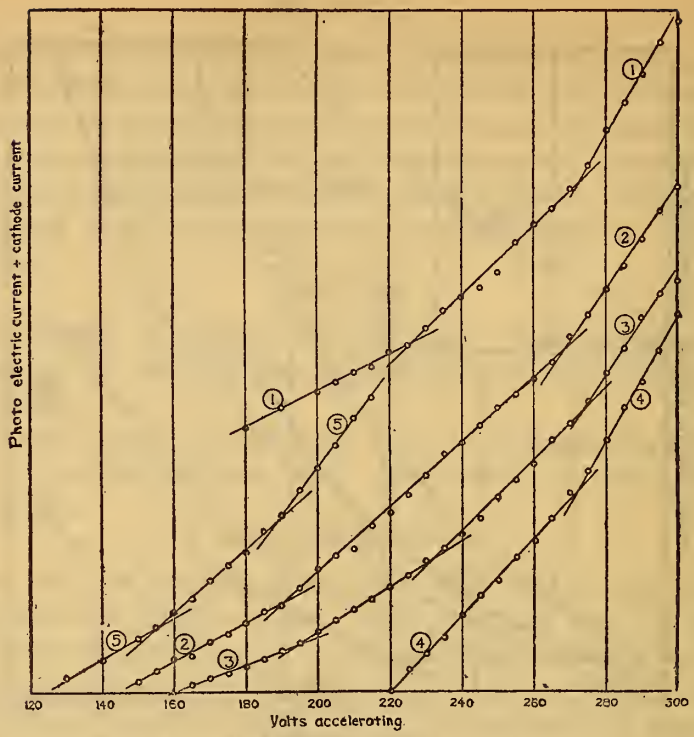

FIG. 6.—*Radiation-voltage curves in carbon monoxide, carbon dioxide, and carbon tetrachloride*

TABLE 5.—Carbon Compounds in Fig. 6

Number	Compound	Pressure or temperature	Observed points	Correction
			Volts	
1	CO	0.70 mm	225 272	.....
2	CCl_4	−73° C	190 270	+1.2
3	CCl_4	−60° C	194 230 274	+1.2
4	CO_2	0.75 mm	273	.....
5	CCl_4	−65° C	155 190	+1.2

CO

Results from 10 curves give inflections at 272.6 ±1.8; 6 curves also show a point at 229 ±3.

CO_2

Results from 8 curves give point at 273.6 ±1.9; 6 curves also show point at 234 ±2. A curve through the mean of 5 series indicates points at 272 and 235; 3 curves in low-voltage range show points near 75 and 100.

C_2H_2

Results from 4 curves show inflections at 269.5 ±0.5; 5 curves show inflections at 237 ±2. While the mean errors happen to be small, the probable error must be large, as the inflections were always faint. Three curves in low-voltage range show inflections near 75 and 110.

CCl_4

Correction +1.2 for potential across cathode. Results from 12 curves show inflection at 270.9 ±1 corrected; 12 curves give 236.2 ±2.2; 14 curves give 197.8 ±3; 2 curves give 157 ±2.

CARBON POINTS FROM ALL COMPOUNDS

271.9 ±1.9, 34 curves; 234.3 ±3.2, 29 curves; 75. approx., 6 curves.

CHLORINE POINTS

197.8 ±3, 14 curves; 157 ±2, 2 curves.

7. AIR

The study of air was for the purpose of measuring critical potentials of nitrogen. With the voltages used, sparking is avoided only by keeping the pressure low. In spite of the pressure being so low it was possible to find conditions that gave very definite inflections in the curves.

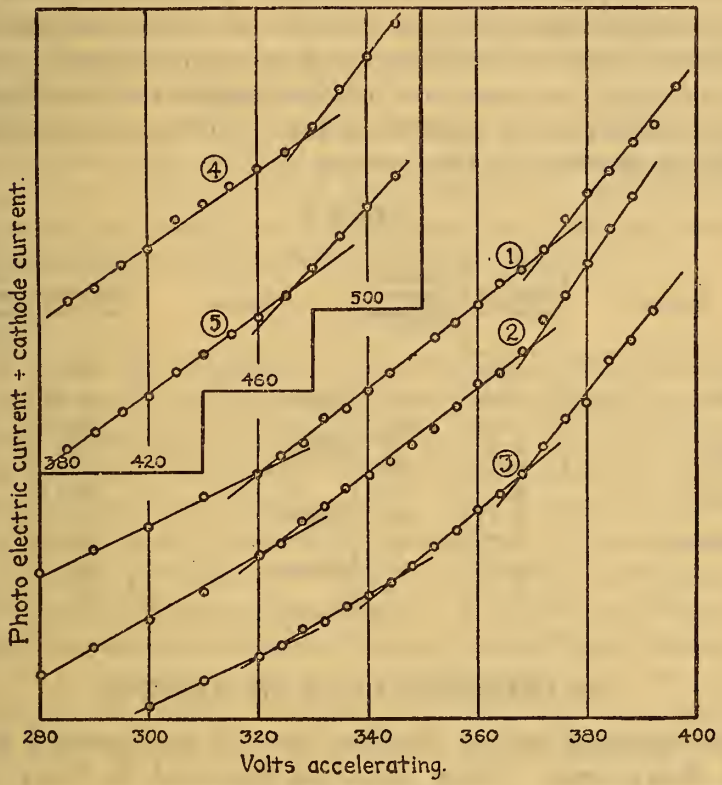

FIG. 7.—*Radiation-voltage curves in air (lower scale) and oxygen (upper scale)*

TABLE 6.—Air and Oxygen Curves in Fig. 7

Number	Pressure	Observed points	Remarks
	mm	Volts	
1 air	0.065	320 372	.....
2 air	.062	320 369	.....
3 air	.060	345 368	.....
4 oxygen	.02	477	.....
5 oxygen	.02	478	Mean of 3

NITROGEN

Twelve curves show a point at 368 ±2.5. All curves show lower points in a range between 310 and 350. Two curves of mean of 5 series each show three separate inflections as follows:

No. 1	311	353	375
No. 2	311	350	373

The mean of separate curves at 368 volts is evidently too low owing to the unresolved effect at 350. The probable value is 374 ±5.

OXYGEN

Three curves show a point at 477 ±2. The curve of the mean of these series gives 478 volts.

8. OXYGEN

Very low pressures were necessitated to avoid sparking. The results here given are only preliminary and are subject to considerable error because of the few curves taken. (See Table 6.)

Table 7 gives a summary of the observed critical potentials and the wave lengths computed from these. Fractions of volts have been omitted throughout, as they are of doubtful significance. The errors given are the mean errors in round numbers. Where none is given, the mean error has been judged too small because of systematic error or insufficient data. All values are probably subject to error of less than 5 volts.

TABLE 7

Element	Observed potentials	Corresponding wave length λ in A	Element	Observed potentials	Corresponding wave length λ in A
	Volts			Volts	
Potassium	19 ±1	650	Sulphur	122 ±1	101
	23 ±1	537		152 ±3	81.2
Sodium	17 ±2	725	Carbon	75	165
	35 ±2	353		234 ±4	52.7
Magnesium	33	374		272 ±2	45.4
	46 ±1	268	Chlorine	157	78.6
Phosphorus	95	130		198 ±3	62.3
	110	112	Nitrogen	352	35.1
	126 ±1	98.0		374	33.0
	163	77.1	Oxygen	478	25.8

IV. INTERPRETATION OF RESULTS

The following section identifies most of the observed points with X-ray series. Other potentials unrelated to X-ray series may be expected on account of multiple ionization. In none of these polyvalent elements except magnesium is there at the present time means for predicting such critical potentials.

We here use the term X-ray to denote radiation from any ring except the outer valence ring. In the case of monovalent alkali metals critical potentials above the first ionization points are accordingly due to ejection of electrons from X-ray rings and are proportional to the limiting frequency of X-ray series. Recent theories of atomic structure generally assume that the elements in the first row of the periodic table have two electron levels, in the second row three electron levels, in the third and fourth rows four electron levels, etc., corresponding to the series 2, 8, 8, 18, 18, 32 in

maximum number of electrons for each level. In the simple Bohr theory these levels may represent coplanar orbits, in more extended theories groups of crossed elliptical orbits, in the Lewis-Langmuir theory shells. Hence the X-ray spectra of the first row of elements should show only the K series, the second row K and L series, the third and fourth rows K, L, and M series, etc. The fact that there are several L and M series is explained in part by Sommerfeld as due to the existence of quantized orbits of slightly different energy value.

The radiation potentials here observed in sodium and potassium may be accordingly ascribed to the L and M series, respectively. It is possible to compute from X-ray data the L series limits for elements in the second row from magnesium to chlorine, using the Kossel relation[10] employed by Duane and Shimizu:

$$La_1 = Ka - K\alpha_1$$

where La_1 is the frequency of the principle L absorption limit, Ka the K limit, and $K\alpha_1$ the strongest K emission line. This relation corresponds to the combination law of line spectra in the visible and ultra-violet, and it is safe to assume that it holds throughout the entire spectral range. Table 8, column 4, gives the wave lengths thus computed for the elements of the second row and the corresponding potentials. The observed potentials are seen to be in fair agreement. There is an experimental error in the points computed from X-ray data comparable to that in the observed potentials because La is the difference of two frequencies of the same magnitude. The per cent error in the X-ray measurements is multiplied about twentyfold in the resulting La value.

TABLE 8.—L Limits

Atomic number	Element	Observed potential	La_1 λ in A	Computed potential	Observed potential	La_5 λ in A	Computed potential
11	Sodium	35			17		
12	Magnesium	46	263.2	46.9	33	421.9	29.3
13	Aluminum		177.6	69.5		251.9	49.1
15	Phosphorus	126	92.2	134	95		
16	Sulphur	152	77.1	160	122	99.9	123
17	Chlorine	198	61.9	199	157		

K limits from measurements of Fricke, K lines from Siegbahn and Hjalmar, as given by Duane, Bull. N. R. C., 1 part, 6, p. 383, 1920.

[10] Phys. Rev., 14, p. 67; 1919.

A characteristic property of X-rays is the Mosely law, that the square root of the frequency of corresponding X-ray lines or limits when plotted against the atomic number gives approximately a straight line. The results for the *La* limit are so plotted in Fig. 8, upper curve. The solid points are computed from X-ray data, the circles from observed potentials. The difference between

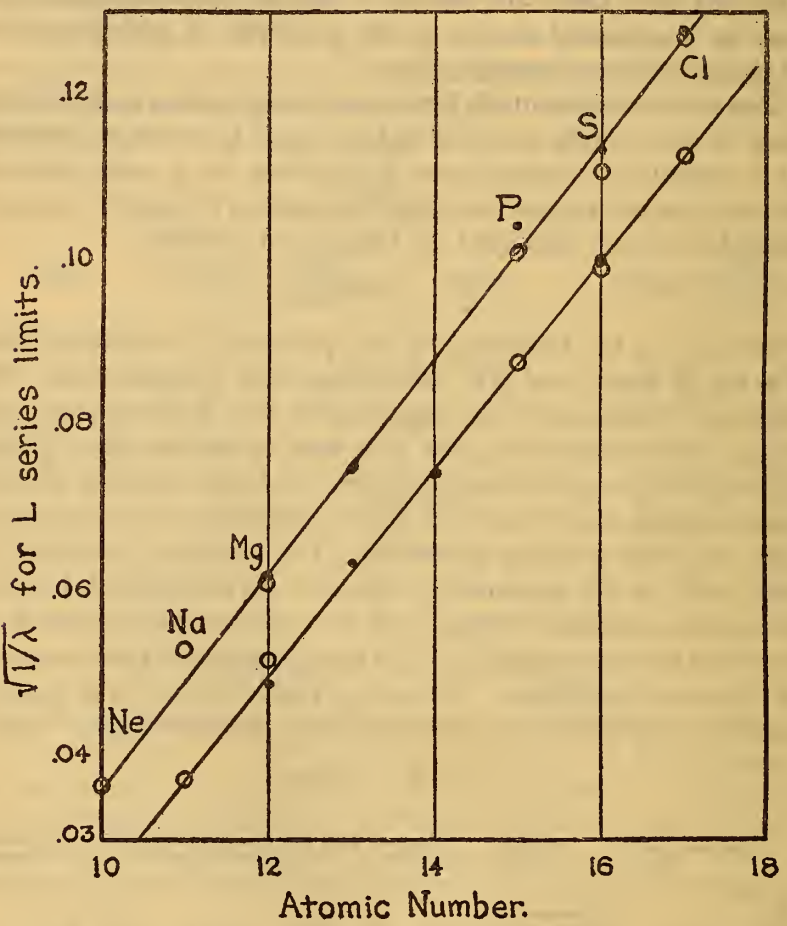

FIG. 8.—*The L-series limits for light elements*

the observed sodium point and the extrapolated straight line is greater than the probable error.

That there is an actual deviation from Mosely's law is confirmed by the results announced by Millikan from measurements of the extreme ultra-violet spectrum of sodium. He finds two isolated lines at $\lambda = 372$ and 376 A which are probably the doublet $L\alpha_1$ and $L\alpha_2$. The line 372 A corresponds to a potential of 33.2

volts, and the L limit is, of course, higher than this. The $L\alpha$ lines must be due to the valence electron falling into the L ring with an energy loss of 33 volts. Ejection of the L electron must require $33+5=38$ volts. Our observed value of 35 volts is thus probably too low rather than too high.

The deviation of the observed sulphur point is large, but the conditions for measuring this potential were unsatisfactory. The straight line between the other points is, within the estimated precision of the method, coincident with the best line through computed points.

We have included in this plot the observed first ionization potential of neon[11] at 16.7 volts, which falls exactly on the L-limit line. A similar relation has been pointed out by Kossel,[12] but he has computed the $L\alpha$ lines and used the neon point observed by Franck and Hertz at 16 volts, assuming this to be the first resonance potential.

In each of the elements of the second row a lower, relatively faint critical potential was also observed. These points plotted on the Mosely scale (lower line in Fig. 8) fall on a straight line nearly parallel to the La_1 line. The determination of these latter potentials was subject to larger errors, and the origin of the sodium point is doubtful, but the combined results seem significant. It is possible to compute from X-ray data a line nearly coincident with this. In these light elements alone a group of lines $K\alpha_3$, $K\alpha_4$, $K\alpha_5$, and $K\alpha_6$[13] have been observed. The frequencies $La_5 = Ka - K\alpha_5$ have been computed and are plotted as dots on the lower curve of Fig. 8. Table 8, right side, gives the computed wave lengths and potentials, as well as the observed points. The frequencies La_3 and La_4 fall closely together and about midway between the two lines drawn. The 110-volt point for phosphorus may be $La_{3,4}$. The computed interval $La_{,1} - La_4$ is 15 volts and the observed interval $126-110=16$ volts. In fact, we should expect a group of limits La_1, La_2 . . . . La_6, of which the first two are predominant. The pairs 1 and 2, 3 and 4, and 5 and 6 are unresolvable. The exceptionally smooth phosphorus curves showed three separate inflections, which is entirely in accord with the above prediction. For the other elements the greater experimental errors may explain the failure to resolve the inflection due to $La_{3,4}$.

[11] Horton and Davies, Proc. Roy. Soc., 98, p. 124; 1920.
[12] Zeit. f. Phys., 2, p. 470, 1920.
[13] From data of Siegbahn and Hjalmar, as given by Duane, Bull. N. R. C., 1 ,p. 383; 1920.

The critical potentials of carbon at 272, air 374, and oxygen 478 volts can be safely ascribed to the *K*-series limits for carbon, nitrogen, and oxygen. The evidence for this lies in part in the fact that the square root of the computed frequency plotted against atomic numbers is a straight line, as shown in Fig. 9. This line intersects the limiting frequency for helium computed from its ionization potential, 25.6 volts,[14] a relation analogous to that of neon in the *L* series. The other line in Fig. 9 is extrapolated from the *K*-series limits observed for magnesium and higher elements. The experimental points for nitrogen and oxygen fall close to this

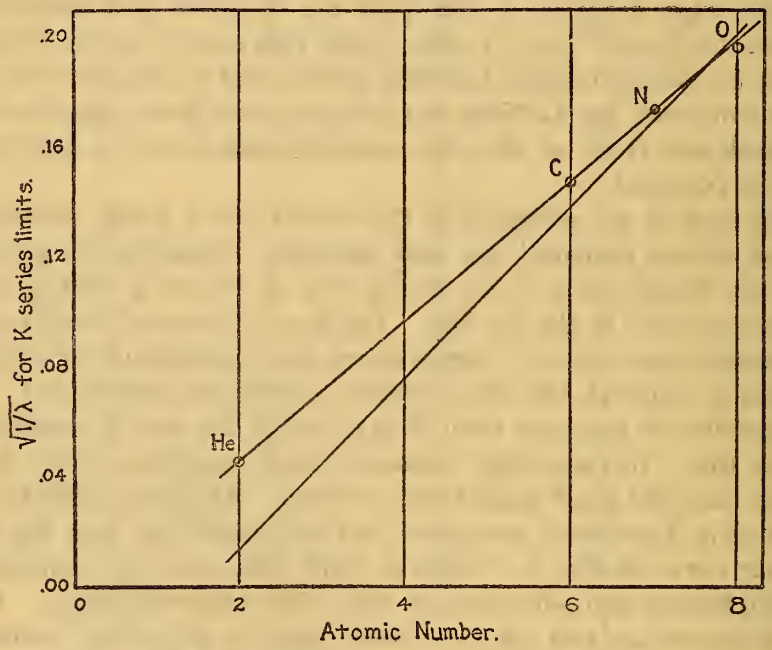

FIG. 9.—*The K series limits for carbon, nitrogen, and oxygen*

line, but the slope given by the three observed points is evidently much less. This indicates that there must be a bend in the *K* line between oxygen and magnesium.

Kurth[15] has detected critical potentials for radiation from solid carbon and oxides at $\lambda = 43.6$ and 23.8 A, respectively. The corresponding values here found are 45.4 and 25.9. The agreement is fair. Hollweck[16] has estimated the *K* limit of carbon from the absorption of thin cellulose films for radiation from a solid anode. He gives 300 volts or 41 A, but this experiment was sub-

[14] Horton and Davies, Phil. Mag. 39, p. 592; 1920.
[15] Loc. cit.
[16] C. R., 172, p. 439; 1921.

ject to much greater error than our critical potential measurements.

The two potassium points observed at 19 and 23 volts have been ascribed to the M series. It is impossible to extrapolate this series with any certainty. The relation

$$Ma = Ka - K\beta$$

gives deviations in Ma of the same order as its magnitude. All we can conclude is that the observed potentials are of the proper magnitude. It is evident that the M-series line through 19 volts will fall close to the ionization potential of argon at 15 volts, in analogous relation to the helium terminus for the K line and the neon terminus for the L line.

V. SOFT X-RAYS FROM SOLIDS

The following description of some work on the radiation from solids at low voltages is included on account of its significance in connection with the work with gases: A four-electrode tube, designed somewhat like that shown in Fig. 1, was used. The inner grid or target was an open spiral closed at the bottom by a rod of the same diameter about 5 mm below the cathode. The outer and inner grids were mounted closely together and the plate was shielded from ions in the residual gas by the same method as before. The open-grid part of the anode served to shield the cathode from the retarding field, so that the cathode current in high vacuum approached saturation at low voltage. The small outer grid confined the discharge in the residual gas to a small volume and so reduced the amount of radiation from gases.

Particular care was taken to secure the best vacuum conditions. A liquid-air trap was mounted between the pumps and vacuum tube, all closely connected by large tubing, and the apparatus was subjected to long baking at 500° C. Pressures were far below the limit of the McLeod gage (0.0001 mm.). The tube used as an ionization gage gave sensitive indications of pressure. Under the best conditions the radiation voltage curves showed no measurable radiation until a critical voltage was reached, at which point the current increased sharply. With cathode currents of over 10 milliamperes the radiation currents were measurable only with full galvanometer sensitivity (10^{-10} amperes).

Fig. 10 shows some results. Curves 1 to 7 were obtained with a nickel anode. Some indicated no measurable current to 80 volts and at this point a definite break. Curve 2 shows a small

current below 80 volts, which is probably due to gas. Curves 5, 6, and 7, however, show a definite break at 60 volts instead of 80. Previously to obtaining curve 5, the cathode temperature had been increased. At the end of the experiment it was found that the anode was coated with tungsten or some substance distilled from the tungsten cathode. Apparently it was the radiation from this coating that was observed in the latter part of the experi-

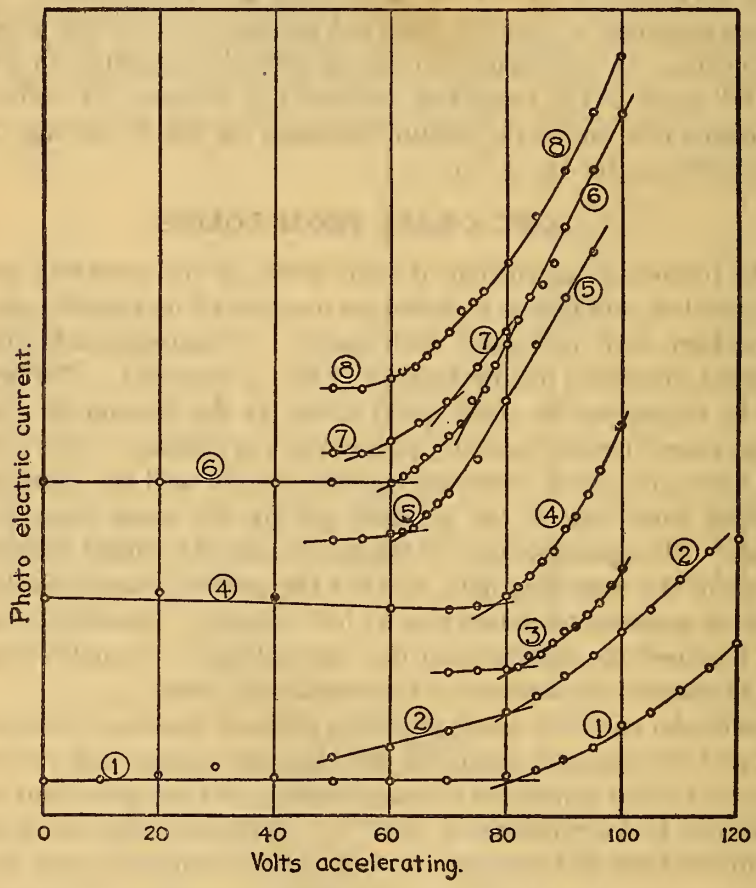

FIG. 10.—*Radiation from solids; nickel and tungsten*

ment. Curve 8, obtained with an iron anode, gives practically identical results as 5, 6, and 7 and probably for the same reason. The sharpness of inflections sometimes obtained with nickel indicates the possibilities of the method. The 80-volt point is probably the *M*-series limit. The 60-volt point can not be safely ascribed to tungsten, as some other distilled impurity may be present, for example, thorium.

Experiments were carried out with a number of metals, but the uncertainty due to surface contamination and difficulty in removing residual gas make the results of questionable value. Aluminum showed an inflection near 70 volts (probably the *L* limit), but there was always evidence of gas radiation starting at low voltage, and the point could not be accurately located.

The result, that under the best vacuum conditions there was no measurable radiation below the first critical potential, should be checked by more sensitive current measurements, as it is contrary to the work of Kurth, who always found general radiation starting at low voltage, as well as characteristic inflections.

The feebleness of the radiation from solids in comparison with that from gases precludes the possibility that the points observed in gases were due to X radiation from the inner grid.

VI. CONCLUSIONS

The present work was undertaken largely to measure the *K* and *L* limits for light elements. The *L* series is most satisfactory as a starting point, since the limits may be computed and results checked. Some general remarks on other aspects of the work follow. The elements of higher valence show evidence of many critical potentials other than X-ray limits, but these are all relatively faint. Apparently under the present conditions of measurement collisions giving multiple ionization were less probable than collisions ejecting one electron from an X-ray ring. There is evidently quite a marked difference in the probability of X-ray excitation in different gases. All these considerations of relative intensity are, of course, uncertain because of the unknown photoelectric sensitivity in this spectral region. But certainly the *L* radiation of sodium is less intense than the *M* radiation of potassium. The *L* radiation of sulphur is likewise relatively weak. Similarly marked differences are observed in the range of X-ray spectral measurements.

Comparison of the results from four different carbon compounds is also of interest. Some atomic theories indicate that X-rays of the same element in different compounds should be of different wave lengths. All four compounds give the same value for the 272-volt point within experimental error of 2 volts, or about 0.3 of an Ångström unit. It is noteworthy that all the points except the two ascribed to chlorine are shown in all the compounds and therefore must be due to carbon atoms.

Some of the results here given are only preliminary. The determination of the beginning of the K series is fundamental to atomic theories, and measurements with the light elements will be carried further. The extensions of the method to the M series and to a search for N and O series in heavy elements is also important. It is seen from the results with gases that a precision of better than 1 per cent was in some cases obtained in the potential measurements.

WASHINGTON, July, 1921.


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